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ELECTROCHEMICAL SYNTHESIS OF BARIUM CUPRATE

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It has been shown that during electrochemical oxidation of copper in solutions of barium hydroxide or in NaOH solutions containing $Ba(OH)_2$ a compound of trivalent copper of type $Ba(CuO_2)_2$ is formed. The formation of insoluble barium cuprate depends on the concentration of hydroxyl ions and barium ions. With sufficiently high concentration of these ions, the yield for current of Cu(III) is the maximum. /181*

Based on the findings it is hypothesized that an extremely unstable trivalent copper oxide or hydroxide is initially formed on the anode, which is stabilized by the hydroxyl ions and barium ions contained in solution.

Barium cuprate can also be produced by exchange reaction of barium ions with electrochemically synthesized sodium cuprate.

The study of anode dissolving of copper in alkaline solutions very rarely draws attention to the formation of trivalent copper compounds. The works of electrochemists [1 - 4] which mention highest oxygen compounds of copper generally mean compounds of peroxide type.

The best proof that copper reaches a trivalent state in anode oxidation is the possibility of producing specific compounds by employing some stabilizing components. Thus, for example, Jirsa [5] and especially Vrtis [6] demonstrated that trivalent copper formed during anode oxidation could be stabilized by tellurates and periodates, and complex trivalent copper salts are formed. In addition, as was apparent from the works of E. Muller [7, 8], trivalent copper isolated on the anode could be stabilized to a certain degree using a high concentration of NaOH (12 - 14 n).

*Numbers in margin indicate pagination in original foreign text.

This work cites data on the possible stabilization of trivalent copper formed during anode oxidation of copper in an alkali solution by barium cations. The work was set up because of the data of Sholder and Voelskow [9], as well as one of us [10] where copper oxidized in an alkali solution was successfully stabilized using hypobromites and hypochlorites, i.e., nonelectrochemically, to a trivalent state using barium and calcium cations.

Experimental Section

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Electrochemical oxidation of copper used copper anodes with area approximately 5 cm^2 covered by electrolytic copper from a copper plating acid bath. Directly before use, the electrodes were steeped in nitric acid and carefully washed with water. A platinum plate served as the cathode. In the same way as E. Muller [7] the anode area was separated from the cathode by a diaphragm which was a No 2 gas filter.

Electrolytic oxidation occurred in a vessel 50 ml in volume usually containing 20 ml of electrolyte. The vessel was covered by a rubber stopper where electrodes and the thermometer were inserted into its hole. In addition a small hole was made in the stopper for removal of oxygen released during electrolysis. Special precautionary measures were not taken to protect the electrolyte from CO_2 entering from the air.

The electrolytic cell was controlled thermostatically, but the solution was not mixed, insofar as it was established that mixing, for example, using a magnetic mixer does not have a perceptible influence on the experimental results.

At the end of electrolysis, the precipitate was separated by centrifuging, after which it was analyzed by the second method we described in [11]. In this method of analysis of barium cuprate, the degree of copper oxidation was somewhat exaggerated, usually no more than by 2 - 3%.

At the same time that the precipitate was analyzed, a determination was made of the quantity of bivalent copper contained in the centrifugate in the form of cuproates, which according to Sholder [12] are compounds of composition $Na_2[Cu(OH)_4]$ or $Ba_2[Cu(OH)_6]$. For this purpose the centrifugate was strongly diluted by water and boiled. As a consequence of hydrolysis, CuO precipitates out of the boiling solution. Within a day after decantation of the transparent solution, the copper content was iodometrically analyzed in the precipitate.

Production of Barium Cuprate Through Sodium Cuprate

A total of 19 n. solution of NaOH was used to synthesize sodium cuprate. This concentrated solution was selected based on preliminary experiments that demonstrated that sodium cuprate in it at a temperature of about 0°C is very stable, and namely does not break down for several months. For electrochemical synthesis of sodium cuprate about 30 ml of 19 n. solution of NaOH was taken, anode density of the current was about 20 a/dm^2, the temperature of the electrolyzed solution was 16 - 25°, the duration of electrolysis 4 hours. The viscous anolyte was mixed using a magnetic mixer. The electrolyte heated during synthesis was cooled by ice water.

Under these conditions almost all the copper precipitating was trivalent. This is apparent from Table 1. Judging from the weight loss of the anode, the yield of Cu (III) for current was close to 9%.

It should be noted that the chestnut sodium cuprate precipitate is formed at higher temperatures, on the order 50 - 55°, and with lower current densities, for example, even at 1.5 a/dm², however with this type of deviation from our selected mode a sharp decrease in Cu (III) yield for current is observed.

In order to obtain barium cuprate, 10 ml of a saturated solution of $Ba(OH)_2$ or 10 ml of a solution of barium chloride of concentration 20 g/l $BaCl_2 \times 2\ H_2O$ was added to 5 ml of a dense suspension of chestnut sodium cuprate in 19 n. of solution of NaOH containing about 15 mg of Cu (III) and over 1 mg of Cu (II), and the mixture was intensively cooled by ice water. Mixing of these components results in the formation of a characteristic chestnut-red barium cuprate precipitate. When it is centrifuged it is easy to note that the centrifugate is stained an intensive blue color. /183

TABLE 1. CONTENT OF TRIVALENT COPPER IN SODIUM CUPRATE AND BARIUM CUPRATE OBTAINED FROM IT

% Content of Cu(III)	In Sodium Cuprate	In Freshly Prepared Barium Cuprate from Sodium Cuprate Under the Influence of		
		Solution on Suspension		Of Saturated Solution of $Ba(OH)_2$ on Sodium Cuprate Precipitate
		$Ba(OH)_2$	$BaCl_2$	
In precipitate	98	95	99	90
in relation to all electrochemically released copper	90	57	53	80

Barium cuprate was also formed by adding 10 ml of saturated solution of $Ba(OH)_2$ to the centrifuged sodium cuprate precipitate.

It is apparent from Table 1 that under the influence on the suspension of sodium cuprate of solutions of barium compounds there is partial breakdown of trivalent copper, however the formed bivalent copper is dissolved in the alkali, forming cuproate, and therefore almost all the copper in the precipitate is trivalent.

Under the influence of a saturated solution of $Ba(OH)_2$ on the precipitate Cu (III) it is broken down noticeably more weakly, however because of the lower alkalinity of the solution, the formed barium cuprate is slightly more contaminated by bivalent copper.

It should be noted that with interaction of sodium cuprate and diluted solution of $BaCl_2$, barium cuprate is not formed. Consequently in order for the exchange reaction to occur successfully, it is insufficient to introduce barium ions, their concentration is important as well as the corresponding alkalinity of the solution.

Synthesis of Barium Cuprate by Direct Electrochemical Copper Oxidation

Anode oxidation of copper in solution of $Ba(OH)_2$. For direct synthesis of barium cuprate, electrolytic oxidation of copper in 30 ml of saturated $Ba(OH)_2$ solution was conducted for 30 - 60 min.

It is apparent from Figure 1 that during synthesis at electrolysis temperatures on the order of 60 - 80°C, all copper in the precipitate is in the trivalent state; with a drop in temperature, the degree of copper oxidation gradually decreases (curve 1). An even /184
stronger change in temperature influences the yield of Cu (III) for current (curve 2). It is characteristic that with constant temperature, the yield for current of Cu (III) in limits 4 - 20 a/dm^2

does not depend on current density (Figure 2). Therefore curve 2 in Figure 1 corresponds to the data of the entire studied interval of current densities.

It should be noted that at high temperatures with an increase in current density the slight yield in Cu (II) noticeably diminishes.

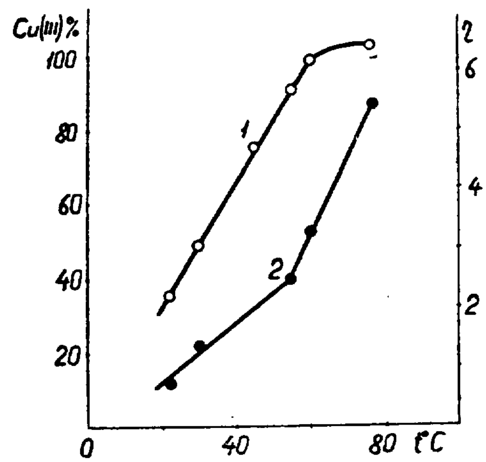

Figure 1. Dependence on Temperature of Electrolyte, Saturated Solution of $Ba(OH)_2$

Key:
1. percentage content of Cu (III) in precipitate
2. yield of Cu (III) for current in %

During electrolytic oxidation of copper in a solution of $Ba(OH)_2$ especially if the solution is hot, one can observe how the oxygen rapidly released on the anode removes chestnut-red flakes of barium cuprate. However sometimes the compounds of trivalent copper are not successfully separated and the anode is covered by a film which,

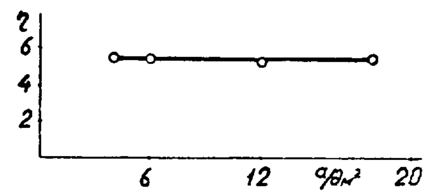

Figure 2. Dependence of Yield for Current Cu (III) on Current Density with Anode Oxidation of Copper in Saturated Solution of $Ba(OH)_2$ at Temperature 70 - 80°C

by the way, is easily scraped off or shaken off. Cases have been observed, however, when the film of trivalent copper cover the anode by a very dense layer, leading to mechanical passivation of the anode.

Increased yield of trivalent copper for current with rise in temperature of barium cuprate electrosynthesis is apparently related to the increased alkalinity of the solution or barium ion concentration. This hypothesis was verified by experiments described below.

Anode oxidation of copper[1] in NaOH solutions containing $Ba(OH)_2$. Alkaline solutions of varying concentration were taken for electrolysis and saturated with barium hydroxide. Thus, the lower the alkaline concentration, the higher the concentration of $Ba(OH)_2$. /185

The data presented in Figure 3 indicate that at 60°C, in a mixture of NaOH and $Ba(OH)_2$ with a concentration of NaOH up to 7.5 n, all the copper in the precipitate is trivalent (curve 2). At 20°,

[1]The authors consider it their duty to express gratitude to the degree student of the chemical dept. of the V. Kapsukas Vilnyus State Univ. Yu. Paulauskayta who participated in some of the experiments described in this section.

the barium cuprate precipitate is not contaminated by bivalent copper, only starting from 5 n of NaOH (curve 1). Then the opposite picture is observed with very high concentrations of NaOH, and contamination of the cuprate by bivalent copper cannot be avoided at any of these temperatures in 15 n. of NaOH.

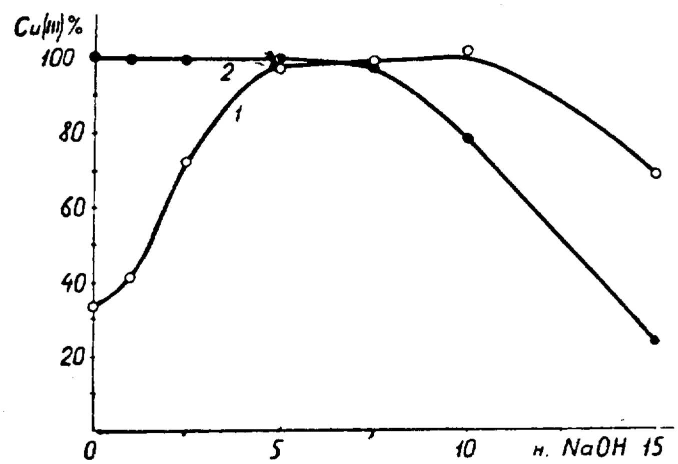

Figure 3. Dependence of Percentage Content of Cu (III) in Precipitate on Alkalinity of Solution of NaOH Saturated by Barium Hydroxide

Key:
1. at 20
2. at 60°C

The results obtained with synthesis of barium cuprate in 15 n of NaOH should be discussed in more detail. The fact is that in these concentrated alkalis, barium cuproate precipitates out, which can even be observed visually. With slow centrifuging of the mother liquor obtained after electrosynthesis, two layers of precipitates settle out: a thin chestnut-red layer of cuprate, and under it a layer of greenish-blue barium cuproate. The data presented in Table 2 from especially conducted experiments demonstrate that with a decrease in quantity of $Ba(OH)_2$ in NaOH solution, the quantity of bivalent copper in the precipitate in the form of cuproate diminishes, and correspondingly increases in the solution.

The aforementioned fact (Figure 3) of contamination of barium cuprate by bivalent copper during electrosynthesis in the 0.0 - 2.5 n solution of NaOH at 20°, and the absence of this at 60° becomes understandable based on the data of Table 3: at 20° the yield of Cu (II) is considerably higher than at 60°, as a result of which not all the copper released from the anode succeeds in being dissolved in relatively lower concentrated alkalis.

Data presented in Table 3 promote a clarification of the optimal conditions for barium cuprate formation. The positive /186
influence of growth in ion concentration OH^- at 20° becomes obvious. However at 60°, growth in OH^- concentration up to 7.5 n essentially does not influence the yield of Cu (III). Consequently under these conditions increased concentration of barium ions or simply temperature itself has a positive influence on the yield of Cu (III).

TABLE 2. RESULTS OF ANALYZING ANOLYTE WITH ELECTROCHEMICAL OXIDATION OF COPPER IN 15 n OF NaOH SOLUTION WITH ADDITION TO IT OF DIFFERENT QUANTITIES OF $Ba(OH)_2$

1 Температура в °C	2 Добавлено $Ba(OH)_2$ в г	3 Доля Cu(III) в осадке в %	Cu(III)	Cu(II) в фугате 4	Cu(II) в осадке 5	Всего 6 Cu(II)	Всего 6 Cu	Выход по току 7 в %	
			в мг 8					Cu(III)	Cu(II)
20—22	0,4	35,3	7,4	12,9	13,6	26,5	33,9	1,5	3,7
	0,16	63,2	11,5	16,0	11,5	27,5	39,0	2,3	3,8
60	0,9	15,5	3,2	5,4	18,2	23,6	26,8	0,7	3,3
	0,16	33,5	3,3	21,5	6,5	28,0	31,3	0,7	3,9

TABLE 2. Continued:
0.6 a (12 a/dm²) was passed in 1 h.

Key:
1. temperature in °C
2. addition of $Ba(OH)_2$ in g
3. percentage of Cu (III) in precipitate in %
4. in centrifugate
5. in precipitate
6. total
7. yield for current in %
8. in mg

TABLE 3. DEPENDENCE OF YIELD FOR CURRENT OF ALKALINITY OF SOLUTION (continued next page)

н. NaOH 1	2 Выход по току в % при			
	20° C		60° C	
	Cu (III)	Cu (II)	Cu (III)	Cu (II)
0,0	0,7	0,9	3,3	0,1
1,0	1,1	1,2	4,5	0,2
2,5	1,9	1,5	4,7	0,6
5,0	4,5	2,1	5,0	1,1
7,5	4,9	2,3	4,9	1,2
10,0	5,8	0,3	3,3	2,7
15,0	2,3	3,8	0,7	3,3

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TABLE 3. Continued:
(0.6 a (12 a/dm^2) passed in 1 h)
Key:
1. n.
2. yield for current in % at

TABLE 4. DEPENDENCE OF RESULTS OF ANODE OXIDATION OF COPPER ON TEMPERATURE WITH VARYING CONCENTRATION OF $Ba(OH)_2$ in 7.5 n of NaOH SOLUTION (continued next page)

1 Температура опыта в °C	2 Раствор NaOH, насыщенный $Ba(OH)_2$ при температуре в °C	3 Доля Cu(III) в осадке в %	В мг 4			Выход по току в % 5		
			Cu(III)	Cu(II)	Cu(III) + Cu(II)	Cu(III)	Cu(II)	Cu(III) + Cu(II)
0	0	97	15,2	31,0	46,2	3,2	4,3	7,5
20	20	99	23,3	17,7	41,0	4,9	2,5	7,4
40	20	100	16,4	17,6	34,0	3,4	2,5	5,9
	40	99	23,4	8,7	32,1	4,9	1,2	6,1
60	20	70	16,0	18,7	34,7	3,3	2,6	5,9
	60	98	23,2	9,3	32,5	4,8	1,3	6,1
80	20	28	3,0	27,5	30,5	0,6	3,9	4,5
	80	40	12,7	16,9	29,6	2,6	2,4	5,0

TABLE 4. Continued:
(0.6 a (12 a/dm^2) passed in 1 h)
Key:
1. experimental temperature in °C
2. solution of NaOH, saturated with $Ba(OH_2)$ at temperature in °C
3. percentage of Cu (III) in precipitate in %
4. in mg
5. yield for current in %

The question of the influence of these factors has been solved in additional experiments whose results are presented in Table 4. It is apparent from them that decrease in concentration of barium ions causes a decrease in yield of Cu (III) and a corresponding increase in the quantity of Cu (II). The influence of temperature which is positive to a certain degree consists only of increase in solubility of $Ba(OH)_2$ with temperature. /187

High temperature in itself has more likely a negative influence on stability of cuprate ion, even barium cuprate in precipitate breaks down more rapidly with a rise in temperature. This follows, for example, from the fact that at 60° with insufficient concentration of barium ions, despite the greater solubility of Cu (II) and its same quantity in anolyte as at 20°, before precipitate, in contrast to the experiment for oxidation at 20° is contaminated by bivalent copper. A similar phenomenon is observed at 80° in the NaOH solution saturated by barium ions. The bivalent copper that does not succeed in being dissolved under these conditions more likely was formed (in the form of CuO) only as a result of breakdown of barium cuprate. The lack of anolyte mixing naturally must foster the accumulation of bivalent copper that has not successfully been dissolved.

During electrolytic oxidation of copper in very concentrated solutions of NaOH containing $Ba(OH)_2$, for example 7.5 n, the yield for current of Cu (III) to a definite maximum magnitude of current density depends somewhat on it (Figure 4), in contrast to electro- /188 synthesis of saturated solutions of $Ba(OH)_2$ without NaOH. It should be noted that a similar, but noticeably more distinct dependence on current density was observed with production of sodium cuprate in 17 - 19 n of NaOH solutions.

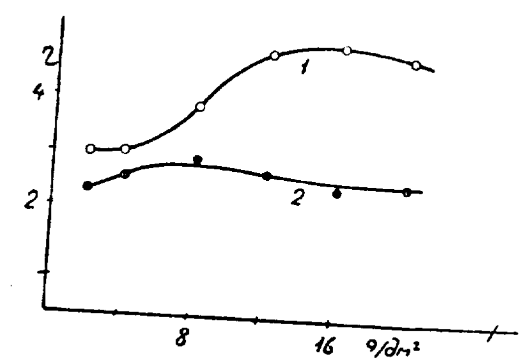

Figure 4. Yield for Current
Key:
1. Cu (III)
2. Cu (II) depending on current density with electrochemical oxidation of copper in 7.5 n of NaOH solution saturated by $Ba(OH)_2$ at temperature 20°

In 7.5 n solutions of NaOH saturated by barium hydroxides, formation of barium cuprate was successfully detected already with current density only slightly higher than 1 a/dm².

In addition to the conditions discussed above influencing electrolytic oxidation of copper, the role of the diaphragm was studied. In working without a diaphragm, the cathode is covered by a loose layer of metal copper. In the experiments the cathode used was a platinum plate of area about 11 cm^2. After electrolysis, the quantities of Cu (III), Cu (II) and on the cathode Cu (O) were defined.

As is apparent from Table 5, during electrolytic oxidation without a diaphragm, the yield of Cu (III) and Cu (II) is considerably lower, the total quantity of released copper changes slightly.

It is thus clear that in conducting electrolysis without a diaphragm, part of the electrochemical oxidized copper is restored on the cathode.

TABLE 5. INFLUENCE OF DIAPHRAGM BETWEEN CATHODE AND ANODE ON BALANCE OF COPPER WITH ELECTROLYTIC OXIDATION OF COPPER IN 7 n SOLUTION OF NaOH SATURATED BY $Ba(OH)_2$ AT TEMPERATURE 20°C AND TRANSMISSION OF CURRENT IN 0.6 a (12 a/dm^2) for 1 h

1 Специфика эксперимента	2 Доля Cu(III) в осадке в %	Cu(III)	Cu(II) в фугате 3	Cu(O)	Всего Cu 4
		в мг 5			
6 С диафрагмой	96	22	17	0	39
7 Без диафрагмы . . .	101	12	12	16	40

Key:
1. specific nature of experiment

(Key continued next page)

TABLE 5. Key continued:
2. Cu (III) in precipitate in %
3. in centrifugate
4. total
5. in mg
6. with diaphragm
7. without diaphragm

Composition of Trivalent Copper Compounds /189

One can currently consider it proven that oxygen compounds of trivalent copper can be released only in the form of anion compounds stabilized by the corresponding cations [9, 13, 14]. This also confirms analyses of preparations obtained by us.

In order to determine their composition, samples of barium cuprate larger than normal were synthesized. For this purpose 120 ml of a 7.5 n NaOH solution saturated with barium hydroxide were taken, and a current of strength 1.4 - 1.6 a was transmitted through it for 3 hours with anode density of the current 14 - 16 a/dm².

The chestnut-red suspension obtained in the anolyte was purified first of $BaCO_3$ and from a surplus of $Ba(OH)_2$. For this purpose the suspension was cooled to 0 - 5° and left in a high closed test tube. The cooled suspension was decanted and centrifuged only to partial precipitation of the sediment. By this means cuprate was freed of $BaCO_3$ and of $Ba(OH)_2$ in the solid phase. In the suspension of barium cuprate remaining and purified of the carbonate part, $Ba(OH)_2$ was removed by centrifuging a suspension heated to 50° with subsequent multiple washing of precipitate on the centrifuge by a 4 n solution of NaOH at room temperature.

In a small part of the precipitate washed of $Ba(OH)_2$, the percentage content of trivalent copper was defined, which makes it possible to calculate Cu: O_{act}. The quantity of active oxygen was defined for a comparison by volumetric method, direct measurement of the volume of oxygen released during hydrolytic breakdown of the resulting preparation in a slightly alkaline solution. In this analysis of active oxygen, the computed degree of copper oxidation was approximately 5% lower than with iodometric analysis.

In order to determine barium, the precipitate washed of $Ba(OH)_2$ was dissolved in 2 n of HCl, barium was precipitated in the form of $BaSO_4$ and its quantity was defined gravimetrically by the generally accepted technique. The filtrate obtained during filtering and washing of $BaSO_4$ was concentrated by evaporation and the total content of copper was iodometrically defined in it.

TABLE 6. RESULTS OF ANALYZING BARIUM CUPRATE

№	Cu(III) в % 1	Cu	Ba	Соотношение Cu : Ba : $O_{акт.}$ 3
		в мг 2		
1	103	47,9	53,0	1 : 0,51 : 0,51
2	106	46,4	53,5	1 : 0,53 : 0,53
3	100	35,6	38,7	1 : 0,50 : 0,50

Key:
1. in %
2. in mg
3. correlation of Cu: Ba: O_{act}

It is characteristic that as a result of fractionation and washing by alkaline, the cuprate was completely purified of admixtures of trivalent copper. Data presented in Table 6 indicate that with anode oxidation of copper a compound of type $Ba(CuO_2)_2$ is formed. Based on these data, as well as based on the studies of Sholder and Voelskow [9] one can consider that with exchange of sodium ions by barium ions in the electrochemically synthesized sodium cuprate, $Ba(CuO_2)_2$ is also produced. There is therefore no /190 doubt that E. Muller in electro-oxidation of copper in a concentrated NaOH solution also produced sodium cuprate and not trivalent copper oxide as he indicated [7].

It should be noted that copper peroxide compounds are not formed in any case of the studied electrochemical oxidation of copper. This is convincingly indicated by the negative results of testing of the corresponding samples for peroxide content.

Discussion of Results

We believe that during anode oxidation of copper, initially trivalent copper oxide or hydroxide is formed. It is most likely that trivalent copper is formed because of oxidation of bivalent copper released on the anode by atomic oxygen. Without delving into the mechanism of the process, one can imagine that oxidation on the anode of bivalent copper to trivalent occurs by the following scheme:

$$2Cu(OH)_2 + O + H_2O \rightarrow 2Cu(OH)_3 \qquad (1)$$

or what is the same

$$4CuO + 2OH^- + O \rightarrow 2Cu_2O_3 + H_2O. \qquad (1a)$$

Trivalent copper hydroxide or oxide is extremely unstable and could only exist on the anode for a very short time, breaking down by the scheme:

$$2Cu(OH)_3 \rightarrow 2Cu(OH)_2 + O + H_2O, \tag{2}$$

if there are no stabilizing agents, for example like barium ions and hydroxyl ions.

With insufficiently high concentrations of barium ions and relatively low alkalinity of the solution, only part of the trivalent copper hydroxide succeeds in reacting with $Ba(OH)_2$ by the scheme

$$2Cu(OH)_3 + Ba(OH)_2 = Ba(CuO_2)_2 + 4H_2O \tag{3}$$

with the formation of more stable barium cuprate; the remaining part of $Cu(OH)_3$ breaks down, or the microzone of the anode is rapidly depleted of barium ions, while the new ions do not succeed in diffusing towards the anode.

With an increase in barium ion concentration, a more significant part of the formed trivalent copper becomes cuprate. The presence of barium ions at the anode means that trivalent copper is stabilized directly on the anode. This, as already mentioned above, can be observed visually with electro-oxidation of copper in a saturated solution of $Ba(OH)_2$ without NaOH.

With a rise in the concentration of hydroxyl ions with introduction of NaOH, the role of barium ion concentration gradually diminishes, insofar as the intermediate product could be formed by sodium cuprate soluble with alkalinity of the solution less than 10 n.

$$Cu(OH)_3 + NaOH = NaCuO_2 + 2H_2O, \tag{4}$$

which undoubtedly is more stable than trivalent copper oxide or /191
hydroxide.

With a strong rise in temperature, stability of sodium cuprate drops sharply and its hydrolytic breakdown intensifies:

$$2NaCuO_2 + 2NaOH \rightarrow 2Na_2CuO_2 + {}^1/_2O_2 + H_2O. \tag{5}$$

Therefore with a rise in temperature there should be a natural increase in the stabilizing value of the barium ions.

Starting from 10 n NaOH, sodium cuprate precipitates out into the sediment, and at lower temperatures breaks down slowly. Therefore in this case the stabilizing value of the barium ions is less significant. It would seem than in 15 n solution of NaOH in which solubility of Ba(OH) is relatively low, and moreover there are losses of barium ions as a result of precipitation of barium cuprate, the yield of Cu (III) at 20° should have been similar as in the pure concentrated NaOH. However this is not observed. On the contrary, there is a drop in the yield of Cu (III) as compared to the less concentrated solutions of NaOH containing a greater quantity of $Ba(OH)_2$. It is not excluded that in addition to oxidation of the anode of Cu (II) to Cu (III) there is dissolving in the alkali of bivalent copper formed on the anode

$$Cu(OH)_2 + 2NaOH \rightarrow Na_2CuO_2 + 2H_2O, \tag{6a}$$

$$Cu(OH)_2 + Ba(OH)_2 \rightarrow BaCuO_2 + 2H_2O \tag{6b}$$

with the formation of cuproates Na_2CuO_2 and $BaCuO_2$ or their hydroxy compounds $Na_2[Cu(OH)_4]$ and $Ba_2(Cu(OH)_6]$.

Since in 15 n solution of NaOH containing $Ba(OH)_2$, barium cuproate precipitates out, the process of anode dissolving of bivalent copper is intensified which slows down oxidation of bivalent copper on the anode to a trivalent state. In addition, barium cuproate to some measure could be crystallized on the anode, somewhat impairing the occurrence of the anode processes.

Some data presented in Table 4 support the fact that bivalent copper in solution could appear not only as a result of breakdown of trivalent copper compounds, but to a certain degree, also as a result of dissolving of bivalent copper which has not succeeded in oxidizing to the trivalent state.

As shown by these data, a certain increase in the total content of copper in anolyte with corresponding change in conditions of electrochemical synthesis is not always linked to an increase in yield for current of copper ions. This is explained by the fact that formation of Cu(II) requires 1.5-fold lower current than for formation of Cu (III), in light of the fact that with more intensive dissolving of the "underoxidized" bivalent copper, a greater quantity of copper passes into the anolyte.

This is indicated by increase in the total yield of the anode-dissolved copper with an increase to a definite limit in alkalinity of the solution (Table 3). The latter agrees completely with the generally known fact of intensification in anode processes with a /192 rise in electrolyte alkalinity [15].

With anode oxidation of copper in saturated solution of $Ba(OH)_2$ without NaOH, dissolving of Cu (II) is relatively very slight, therefore under favorable conditions almost all the bivalent copper formed on the anode is oxidized to trivalent.

In addition to the aforementioned processes, part of the barium cuprate can be broken down during electrolysis because of hydrolysis

$$Ba(CuO_2)_2 + 4H_2O \rightleftarrows 2Cu(OH)_3 + Ba(OH)_2, \qquad (7)$$

$$2Cu(OH)_3 \rightarrow 2Cu(OH)_2 + H_2O + {}^1/_2O_2. \qquad (8)$$

In the presence of NaOH, copper hydroxide dissolved by scheme (6a), forming cuproate. In addition, in the presence of NaOH, an exchange reaction [10] could occur:

$$Ba(CuO_2)_2 + H_2O + 2NaOH \rightleftarrows 2NaCuO_2 + Ba(OH)_2 \qquad (9)$$

where the subsequent hydrolytic breakdown of the less stable sodium cuprate formed in solution is similar to equations (7, 8). The resulting summary equation of this reaction is presented in scheme (5). $Cu(OH)_2$ formed by equation (8) could be partially degraded, in this case contaminating the barium cuprate precipitate with copper cupric oxide slowly dissolving in the alkali.

As is apparent from schemes (7) and (9), with fairly high concentration of $Ba(OH)_2$, the process of barium cuprate breakdown must be slowed down, which is confirmed by studies of $Ba(CuO_2)_2$ in alkaline solutions. It has been established that during storing of two similar samples of barium cuprate in 20 ml of a 7 n solution of NaOH saturated by $Ba(OH)_2$ and without $Ba(OH)_2$, at the end of 2 days barium cuprate stored in NaOH without barium hydroxide breaks down more strongly (Table 7).

TABLE 7. BREAKDOWN OF BARIUM CUPRATE SUSPENSION FOR 2 DAYS AT ROOM TEMPERATURE

1 Купрнат бария в 7 н. растворе NaOH	Доля Cu(III) в осадке 4 в %	Cu(III)	Cu(II) в осадке 5	Cu(II) в фугате 6	Всего Cu 8
		в мг 7			
2 Содержащем $Ba(OH)_2$	87	7,1	1,1	8,6	16,8
Без $Ba(OH)_2$	49	2,9	3,0	12,6	18,5

Key:
1. barium cuprate in 7 n solution of NaOH
2. containing
3. without
4. percentage of Cu (III) in precipitate in %
5. in precipitate
6. in centrifugate
7. in mg
8. total

Based on subsequent schemes one could also thus explain the ratio between the established quantities of Cu (III) and Cu (II) depending on the experimental conditions. However the rate of barium cuprate breakdown as is apparent from Table 7 at room temperature is insufficiently high in order to have a decisive influ- /193
ence on the composition of anolyte in the majority of cases of electrolytic oxidation. This breakdown could occur with concentration of $Ba(OH)_2$ insufficient at high temperatures of electrosynthesis, as proven in the discussion of Table 4. With relatively high concentration of barium ions, for example, in pure saturated solutions of $Ba(OH)_2$, even at 80° there is no breakdown of barium cuprate during electro-oxidation. This could explain the weaker breakdown of trivalent copper with the addition of $Ba(OH)_2$ to the released precipitate of sodium cuprate, than with addition of $Ba(OH)_2$ to its very alkaline suspension.

There is no doubt that during electrochemical oxidation of copper all the described processes occur to a certain measure, and dominance of any one of them depends on the electrolysis conditions. In addition, the discussed processes depend on the structure of the anode surface, which somethat deteriorates reproducibility of the experiments.

In conclusion we would like to focus especial attention on the fact that sodium hydroxide added to $Ba(OH)_2$ not only improves the stability of cuprate, but also what is very important, is a dissolver of bivalent copper, as a result of which under less favorable conditions of electrosynthesis, all the copper in the precipitate is in a trivalent state. For this one should only avoid saturation of the alkali by cuproate, which is achieved either by reducing the duration of the electrolysis, or increasing the quantity of electrolyte.

Conclusions

1. A compound of trivalent copper of type $Ba(CuO_2)_2$ was synthesized by anode oxidation of copper.

2. A dependence was established of the formation of barium cuprate during anode oxidation of copper on the alkalinity of the electrolyte, concentration of barium ions in it, as well as temperature and current density.

3. A hypothesis regarding the mechanism of electrochemical formation of cuprate has been advanced.

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16. Abstract

It has been shown that during electrochemical oxidation of copper in solutions of barium hydroxide or in NaOH solutions containing $Ba(OH)_2$ a compound of trivalent copper of type $Ba(CuO_2)_2$ is formed. The formation of insoluble barium cuprate depends on the concentration of hydroxyl ions and barium ions. With sufficiently high concentration of these ions, the yield for current of Cu(III) is the maximum. Based on the findings it is hypothesized that an extremely unstable trivalent copper oxide or hydroxide is initially formed on the anode, which is stabilized by the hydroxyl ions and barium ions contained in solution. Barium cuprate can also be produced by exchange reaction of barium ions with electrochemically synthesized sodium cuprate.

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